

COMPARISON OF SIMULATION AND EXPERIMENTAL ANALYSIS FOR THE SEPARATION OF LIGHT NAPHTHA USING PRESSURE SWING ADSORPTION

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ABSTRACT

This study presents the evaluation of experimental and simulation analysis for the separation of light naphtha using pressure swing adsorption; to provide basic design parameters for the setup of the pilot industrial plants. The Aspen-Adsorim software was employed for the simulation of n-paraffins breakthrough curves in single adsorption tower using equilibrium isotherms, kinetic and energy balance equations parameters gotten from independent laboratory experiments and correlative literatures. The results of this study show that the deviation values of breakthrough time between simulation and experiment were less than 7%, and the isotherms fitting for Langmuir model were higher than 98% for n-pentane and n-hexane on 5A molecular sieve. It is interesting to note that high purity (more than 95.5wt iso-paraffins and more than 99.5wt n-paraffins) products were produced. Another important finding was that the simulated results were in good agreement with the experiments, which can provide basic design parameters for the setup of the pilot industrial plant.

KEYWORDS: Light naphtha, Separation Process, experimental, stimulation.

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INTRODUCTION

Light naphtha are highly volatile, flammable liquid mixtures of hydrocarbons distilled from petroleum, coal tar, and natural gas; which are often used as fuel, as solvents, and in making various chemicals [Henry, 1950; Sun, 2009; Martin *et al*, 1998]. The light naphtha contains about 30wt% n-paraffins, and the rest of others components are iso-paraffins [Henry, 1950; Sun, 2009; Martin *et al*, 1998]. In using the light naphtha for ethylene cracking, the ethylene yield is only about 31% and when used for gasoline blending materials directly, the research octane number (RON) decreases significantly (the RON of iso-pentane is 93 compared with 62 for n-pentane). The n/iso-paraffins in light naphtha can effectively be separated taking the mode molecular management and achieve the best use of n/iso-paraffins; which the pressure swing adsorption processes shows great prospects.

Over the years the Pressure swing adsorption technology are used in a large variety of applications; for example; hydrogen purification [Maleck and Farooq, 1998], air separation [Jee and Lee, 2001], on-board gas generation system [Santos *et al*, 2006], and CH₄ upgrading [Kim *et al*, 2006]. The processes are normally associated to low energy consumption when compared to other technologies, for example cryogenic for gas separation [Mersmann *et al*, 2000]. Interestingly, pressure swing adsorption is preferred to other processes when the concentration of the components to be removed is quite important. In such conditions, loading the column with the heavy component is accomplished quite fast. This is made possible since the pressure of the system can be changed rapidly and the time between adsorption and regeneration is balanced. When the concentration is low, the adsorption step may take much longer and other options like temperature swing adsorption can be considered [Mersmann *et al*, 2000].



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Aspen Adsorption model is a comprehensive flowchart simulator developed for optimal design, simulation, optimization and analysis of adsorption processes. The model enables simulation and optimization for a wide range of industrial gas and liquid adsorption processes. Rodrigues *et al* [Silva, 1998; Jose, 2000; Silva, 1997] on their study on N₂-nC₅-nC₆ system showed the variation of energy and concentration in the pressure swing adsorption simulation process. Zhang [Zhuo *et al*, 2001] proposed a three bed vacuum pressure swing adsorption process used for separating the CH₄-N₂ mixed gas, and the concentration of methane increased from 30% to 60%. This article proposed the use of Aspen-Adsim software to simulate the adsorption-desorption cyclic processes of n-paraffins on 5A molecular sieve using model parameters gotten from independent experiments and correlative literatures.

MATERIAL AND METHODS

Experiment

Materials

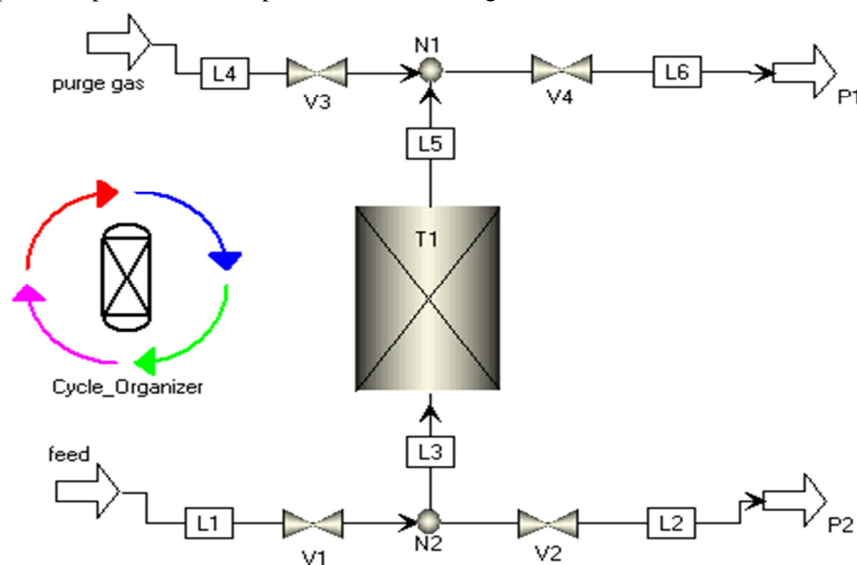
The material used in this experiment is light naphtha (containing about 30wt% n-paraffins). Table 1 shows the main components of the light naphtha.

Table 1: Main components of light naphtha

NO.	components	molecular formula	symbol	boiling point/°C	contents (wt%)
1	2-methyl-butane	C ₅ H ₁₂	2MB	28.0	40.23
2	pentane	C ₅ H ₁₂	NP	36.0	26.94
3	cyclopentane	C ₅ H ₁₀	CP	49.3	1.13
4	2,3-dimethyl-butane	C ₆ H ₁₄	23DMB	58.0	17.41
5	2-methyl-pentane	C ₆ H ₁₄	2MP	60.0	7.78
6	hexane	C ₆ H ₁₄	NH	68.7	4.13
7	methylcyclopentane	C ₆ H ₁₂	MCP	71.8	2.38

Simulation process

The Aspen adsorption simulation process is shown in Figure 1.



(T1-adsorption tower, V1-V4: control valve, L1-L6: material stream, P1/P2: products)

Figure 1: Aspen Simulated process flow chart



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Mathematical models and parameters

Mathematical models

The pressure swing adsorption process for non-isothermal and non-adiabatic model has constant heat of adsorption and heat transfer. The specific model assumptions for the process are:

- (1) The ideal gas law applies.
- (2) The flow pattern is plug flow model, radial concentration is same without axial diffusion, and the pressure drop through the bed conforms to the Ergun equation.
- (3) The kinetic model assumption is lumped resistance, the mass transfer driving force for component 'i' is a linear function of the gas phase concentration (fluid film).
- (4) The adsorption equilibrium is described by Langmuir model.
- (5) The discretization method is Upwind Differencing Scheme 1 (UDS1).

From these assumptions the model equations are stated thus:

Continuity equation:

$$-\varepsilon_i E_{zi} \frac{\partial^2 c_i}{\partial z^2} - \varepsilon_i E_{ri} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) + \frac{\partial (v_g c_i)}{\partial z} + \varepsilon_B \frac{\partial c_i}{\partial t} + j_i = 0 \quad 1$$

Where, ε_i -bed porosity ($\text{m}^3 \cdot \text{m}^{-3}$), E -diffusivity coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), r -bed radius (m), ε_B -total of bed and pellet porosity, v_g -space velocity (m/s), j_i -mass transfer rate ($\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$).

Ergun equation:

$$\frac{\partial p}{\partial z} = \left(\frac{1.5 \times 10^{-3} (1 - \varepsilon_i)^2}{(2r_p \psi)^2 \varepsilon_i^3} \mu v_g + 1.75 \times 10^{-5} M \rho_g \frac{(1 - \varepsilon_i)}{2r_p \psi \varepsilon_i^3} v_g^2 \right) \quad 2$$

Where, μ -viscosity ($\text{Ns} \cdot \text{m}^{-2}$), M - molecular weight ($\text{kg} \cdot \text{kmol}^{-1}$), ψ -adsorbent sharp factor, r_p - pellet radius (m).

The resistances to mass transfer equation:

$$j_i = MTC_i (c_b - c_s) = -\rho_s \frac{\partial w_i}{\partial t} \quad 3$$

Where, j_i is mass transfer rate ($\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$), MTC_i is mass transfer coefficient (s^{-1}), C_i is gas concentration ($\text{kmol} \cdot \text{m}^{-3}$), C_b is gas-solid interfacial concentration ($\text{kmol} \cdot \text{m}^{-3}$), C_s is gas concentration ($\text{kmol} \cdot \text{m}^{-3}$), ρ_s is bulk solid density of adsorbent ($\text{kg} \cdot \text{m}^{-3}$).

Langmuir model equation:

$$w_i = \frac{IP_i P_i}{1 + IP_i P_i} \quad 4$$

Where, IP_i / IP_2 are isotherms parameters, P_i is adsorption pressure (bar), w_i is adsorption weight (kmol kg^{-1}).

The Upwind Differencing Scheme 1 (UDS1) equation is represented as:

$$\frac{\partial \Gamma_i}{\partial z} = \frac{\Gamma_i - \Gamma_{i-1}}{\Delta z} \quad 5$$

The (UDS1) Upwind schemes was use an adaptive or solution-sensitive finite difference stencil to numerically simulate the direction of propagation of information in the flow field.



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Model parameters

Model parameters used in experiment and simulation are listed in Table 2

Table 2: Model parameters used in experiment and simulation

Variables	Values	Units	Description
Hb	600	mm	Height of adsorbent layer
Hb	26	mm	Internal diameter of adsorbent layer
Ei	0.32	m ³ void/m ³ bed	Inter-particle voidage
Ep	0.26	m ³ void/m ³ bed	Intra-particle voidage
RHOs	730	kg/m ³	Bulk solid density of adsorbent
Rp	1	mm	Adsorbent particle radius
SFac	1.0		Adsorbent shape factor
MTC(NP)	25	s ⁻¹	Constant mass transfer coefficients
MTC(NH)	24	s ⁻¹	Constant mass transfer coefficients
IP(1,“NP”)	0.071	Kmol·kg ⁻¹ ·bar ⁻¹	Isotherm parameter
IP(1,“NH”)	0.57	Kmol·kg ⁻¹ ·bar ⁻¹	Isotherm parameter
IP(2,“NP”)	48.45	Kmol·kg ⁻¹ ·bar ⁻¹	Isotherm parameter
IP(2,“NH”)	403.41	Kmol·kg ⁻¹ ·bar ⁻¹	Isotherm parameter
DH(“NP”)	-35.0	MJ/Kmol	Constant for heat of adsorption
DH(“NH”)	-25.0	MJ/Kmol	Constant for heat of adsorption

RESULTS AND DISCUSSION

Figure 3 showed the Langmuir adsorption isotherms model of n-pentane and n-hexane on 5A molecular sieve investigated on IGA-100 at 200 °C.

Figure 4 showed the experiment and simulation breakthrough curves of n-paraffins in light naphtha on fresh 5A molecular sieve under different liquid feed space velocity (1.355h⁻¹, 1.162h⁻¹, 0.968h⁻¹, 0.774h⁻¹ and 0.581h⁻¹). The liquid feed space velocity decreases from 1.355h⁻¹ to 0.581h⁻¹, the breakthrough time deviations between simulation and experiment are 3.85%、3.39%、6.93%、2.5% and 0.76% respectively.

Figure 4 and 5 showed the breakthrough time of experiment and simulation under different liquid feed the simulation results, which are consistent with experimental dates. The mathematical models and parameters are suit for adsorption system, which four adsorption-desorption cycles are simulated. Figure 6 shows the concentration curves of n-pentane and iso-pentane for simulation of adsorption-desorption four cycles (adsorption 900s, desorption 600s). The concentration in adsorption tower reaches a steady state after the second cycle.

Figure 7 shows the temperature change curve of outlet adsorption tower material. As the high adsorption heat of n-paraffins, initial temperature rise of bed is more than 10°C, after the second cycle the outlet temperatures maintain between 198~201°C, while the experimental temperatures keep between 195~205°C.

Figure 8 and 9 shows outlet concentration curves during single cycle of adsorption/desorption when the bed reaches stable states. The breakthrough time of n-pentane is about 210s and n-hexane is 420s. The product are of high purity with more than 95.5%wt iso-paraffins and 99.5%wt n-paraffins) produced.



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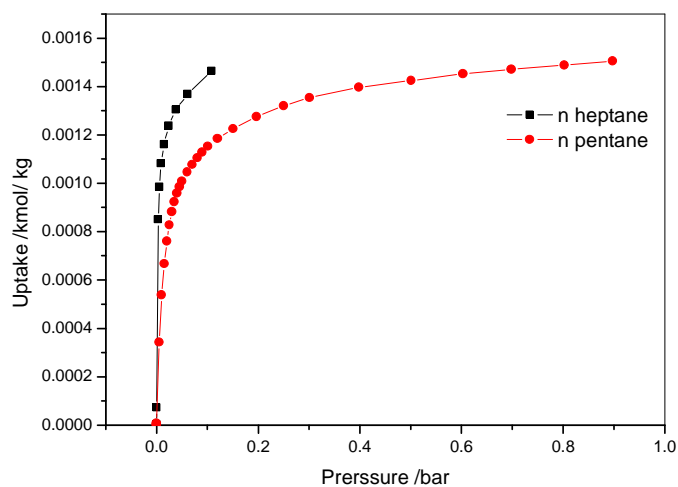


Figure 3: Adsorption isotherms of n-heptane and n-pentane on 5A molecular sieve at 200 °C

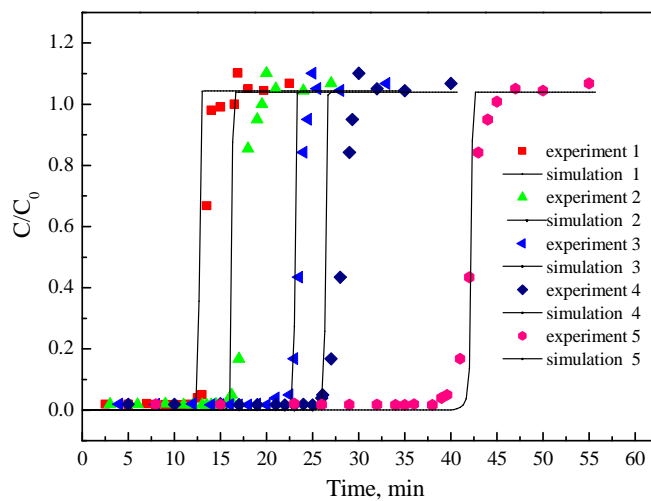


Figure 4: Experiment and simulation breakthrough curves under different liquid feed space velocity (1~5 represent 1.355h^{-1} , 1.162h^{-1} , 0.968h^{-1} , 0.774h^{-1} and 0.581h^{-1})



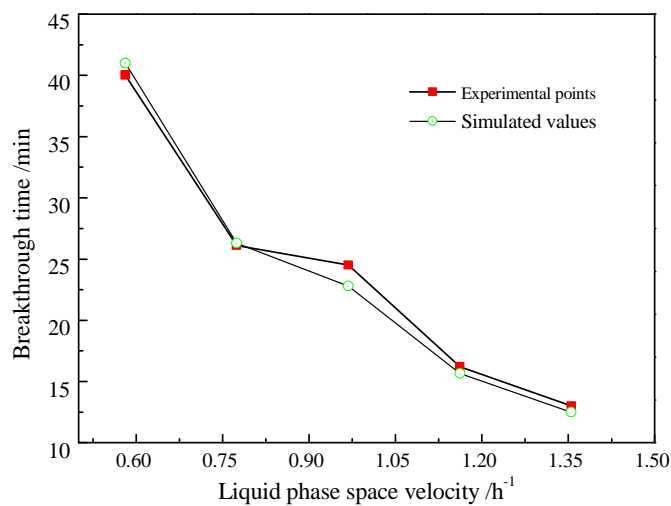


Figure 5: Breakthrough time of experiment and simulation under different liquid feed space velocity

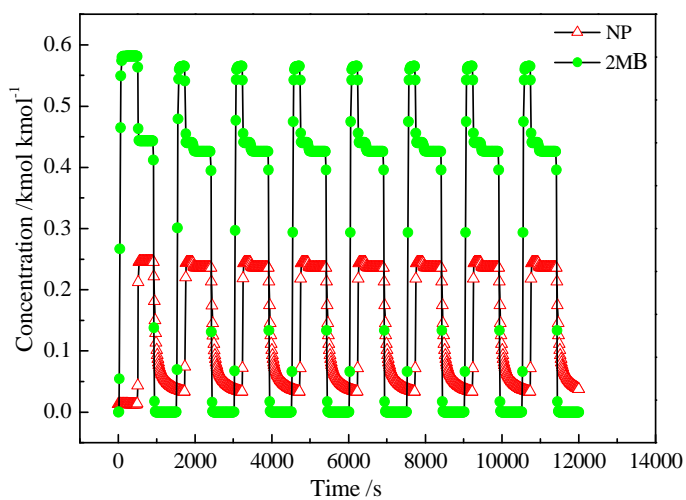


Figure 6: Concentration curves of n-pentane and iso-pentane among four cycles



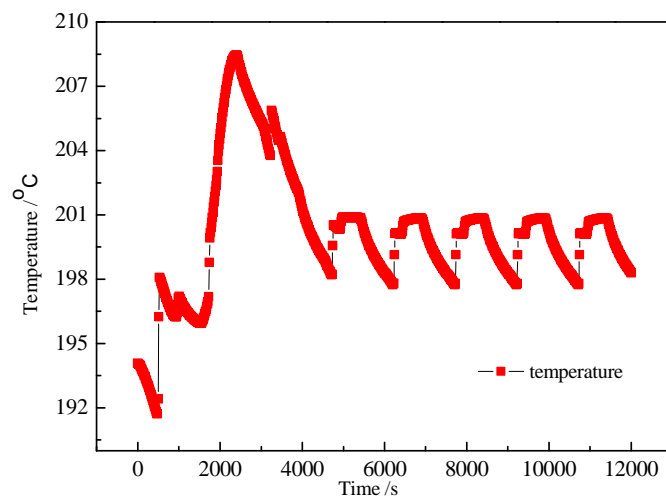


Figure 7: Temperature change curve of outlet adsorption tower material

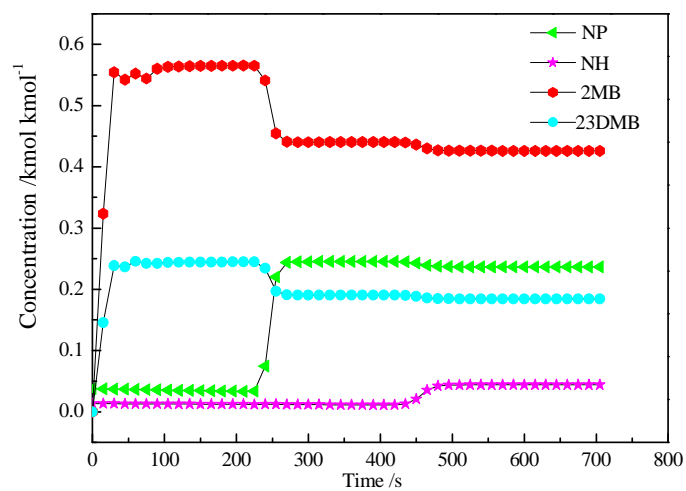


Figure 8: Outlet concentration curves of NP/NH/2MB/23DMB for single adsorption cycle



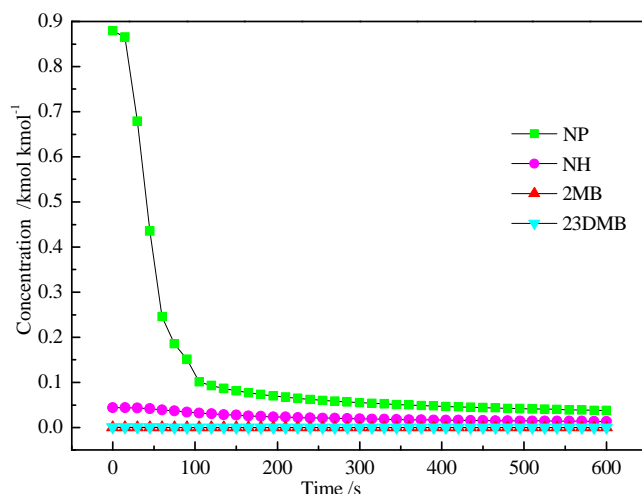


Figure 9: Outlet concentration curves of NP/NH/2MB/23DMB during single desorption cycle

CONCLUSIONS

The isotherms of n-pentane and n-hexane on 5A molecular sieve are identical to Langmuir fitting curves, and the fitting degrees are higher than 98%. The breakthrough curves are in good agreement with the experimental results. The deviation values of breakthrough time between simulation and experiment are less than 7% in single tower. The outlet simulation temperatures of materials are in the range of 198-201 °C, while experimental results are between 195-205 °C; the difference is associated with the energy model selection. Therefore, at stable states, the breakthrough time of n-pentane and n-hexane are 210 and 420 seconds respectively, with high purity (more than 95.5%wt iso-paraffins and more than 99.5%wt n-paraffins) products obtained.

The single tower pressure swing adsorption cycles can be extended to the multi-tower continuous operations, which provide useful guidance for the actual operation. Also, in these growing applications of pressure swing adsorption technology, faster and efficient separations can be achieved through good collaboration between materials science and process engineering.

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